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Hydrodesulfurization of Dibenzothiophene Catalyzed by Alumina-Supported Ruthenium Carbonyl-Alkali Metal Hydroxide Systems

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Catalyst derived from alumina-supported ruthenium carbonyl-alkali metal hydroxide systems remarkably increased the catalytic activity in hydrodesulfurization of dibenzothiophene compared with an alumina-supported ruthenium carbonyl, ruthenium acetylacetonate or ruthenium chloride system to give biphenyl selectively.

Recently, much attention has been focused on deep desulfurization of light oil and development of new catalysts for this purpose has been one of urgent problems. Since it has been reported by Pecoraro and Chianeli1) that ruthenium sulfide is most active for hydrodesulfurization (HDS) among transition metal sulfides, a number of attempts have been made to develop ruthenium catalysts active for HDS,2-5) hydrogenation6) and hydrodenitrogenation.2) Thus, deposition of ruthenium species onto a high surface area support has been expected to exhibit several interesting properties. On the other hand, supported metal carbonyl complexes are found to be active for several catalytic reactions,7) e.g. hydrogenation of carbon monoxide,8) metathesis of olefin9) etc. However, their reactivities for hydrodesulfurization (HDS) of thiophenes, especially dibenzothiophene (DBT) which is a key compound in desulfurization of heavier feedstock such as light oil, have been scarecely investigated.10)

In the present communication, we report HDS of DBT catalyzed by alumina-supported ruthenium carbonyls. It was found that the catalysts derived from alumina-supported $Ru_3(CO)_{12}$-alkali metal hydroxide (MOH) systems, where $Ru_3(CO)_{12}$ reacts with an alkali metal hydroxide to give an anionic ruthenium hydride complex ($MHRu_3(CO)_{11}$: M=alkali metal), exhibited much higher catalytic activity for HDS of DBT than that derived from alumina-supported $Ru_3(CO)_{12}$, ruthenium acetylacetonate ($Ru(AcAc)_3$) and ruthenium chloride ($RuCl_3$) system.

Commercially available $Ru_3(CO)_{12}$, $Ru(AcAc)_3$, $RuCl_3$,and alkali metal hydroxides (LiOH, NaOH, KOH, RbOH,and CsOH) were used without further purification. Typical procedure was as follows: 0.13 mmol of a ruthenium compound and 0-1.2 mmol of an alkali metal hydroxide were dissolved in methanol or water (5 ml) and stirred at 25 °C for 30 min. After the reaction, 0.46 g of gamma-Al_2O_3 (>20 mesh) was added into the reaction mixture and stirred for 2 h. Solvent was removed in vacuo. This catalyst precursor was placed into a pressurized fixed-bed flow reactor (10 mm i.d. x 300 mm) and activated under a flow of 3% H_2S in H_2 at 300 °C for 3 h. HDS of DBT was carried out at 300 °C for 3-10 h (50 kg/cm^2, H_2 18 l/h, LHSV 14 h^{-1}, 1 wt% of DBT in xylene). Products were analyzed by GC with a FID detector. The XPS spectra were recorded by a Shimadzu ESCA-850 with a MgKα ray. The binding energies were referenced to the C1s band at 285.0 eV.

Table 1. Hydroddesulfurization of Dibenzothiophen Catalyzed by Alumina-Supported Ruthenium Catalysts [a)]

Run	Catalyst	Conv. of DBT %	Conv. of DBT to BP %	Conv. of DBT to CHB %	Selectivity of BP %
1	$Ru_3(CO)_{12}/Al_2O_3$	44	38	6	86
2	$Ru(AcAc)_3/Al_2O_3$[b)]	35	30	5	87
3	$RuCl_3/Al_2O_3$	32	23	9	71
4	$Ru_3(CO)_{12}$+3NaOH/Al_2O_3	71	67	4	95
5	$Ru(AcAc)_3$+NaOH/Al_2O_3[b)]	43	40	3	93
6	$RuCl_3$+NaOH/Al_2O_3	15	14	1	95
7	$Ru_3(CO)_{12}/Al_2O_3$+3NaOH[c)]	43	40	3	94
8	3NaOH/Al_2O_3+$Ru_3(CO)_{12}$[d)]	32	30	2	94

a) Temperature 300 °C, Pressure 50 atm, LHSV 14 h^{-1}, Cat 0.5 g, H_2 18 l/h, Amount of $Ru_3(CO)_{12}$ 0.13 mmol; Presulfided by H_2S in H_2 at 350 °C (H_2S 3%). b) AcAc= acetylacetonate. c) Initially $Ru_3(CO)_{12}$ was supported on Al_2O_3 and then NaOH was added at Ru/Na=1. d) Initially NaOH was supported on Al_2O_3 and then $Ru_3(CO)_{12}$ was added at Ru/Na=1.

Alumina-supported ruthenium catalysts were active for HDS and products were biphenyl (BP), cyclohexylbenzene (CHB) and a trace amount of hexahydrodibenzothiophene. The catalytic activities of catalysts derived from alumina-supported ruthenium decreased in the order $Ru_3(CO)_{12}$> $Ru(AcAc)_3$> $RuCl_3$ (runs 1, 2, and 3). When $Ru_3(CO)_{12}$ was reacted with NaOH and then supported on alumina (run 4), the catalytic activity remarkably increased and the conversion of DBT was 71%. At the preparation of the catalyst in this system, $Ru_3(CO)_{12}$ reacted with sodium hydroxide to give $NaHRu_3(CO)_{11}$ quantitatively which was comfirmed by FTIR (2076 (w), 2022 (vs), 1993 (s), 1964(m), 1642(w) cm^{-1}

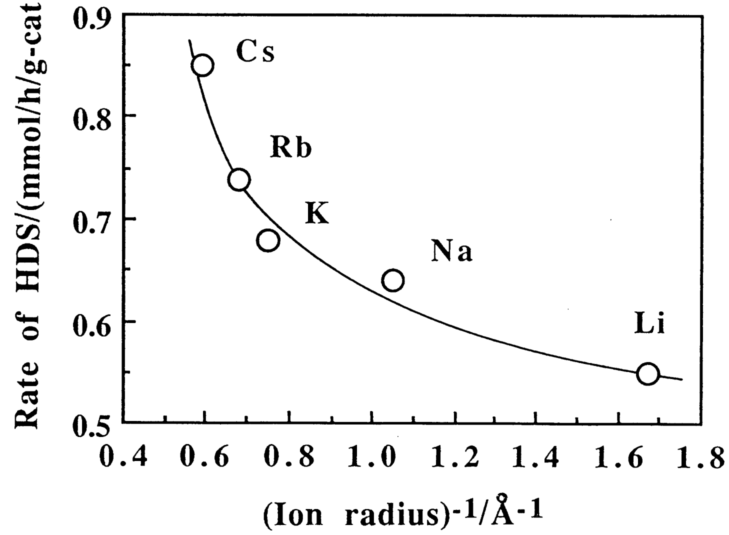

Fig. 1. Rate of DBT HDS vs. (Ion radius)$^{-1}$ $Ru_3(CO)_{12}$+3MOH/Al_2O_3 (M=Li, Na, K, Rb or Cs), 300 °C, 50 kg/cm^2, H_2 18 l/h, LHSV 14 h^{-1}, 1 wt% of DBT in xylene, 3 h on stream.

in methanol.[11] Addition of NaOH into the Ru(AcAc)$_3$ system slightly increased the activity (run 5) while that into the RuCl$_3$ system decreased the conversion of DBT (run 6). When $Ru_3(CO)_{12}$ and NaOH were separately supported on alumina, an significant increase in the catalytic activity was not observed (runs 7 and 8). This indicates that the presulfidation of $NaHRu_3(CO)_{11}$ supported on alumina is instrinsic for the high catalytic activity. Further, the use of alkali metal compounds such as sodium iodide, sodium bicarbonate, sodium sulfate other than NaOH decreased the catalytic activity while the use of sodium sulfide and sodium acetate did not reveal the remarkable change in the catalytic activity and the selectivity for biphenyl. It is suggested that the catalytic activity in HDS did not increase since these compounds can not react with $Ru_3(CO)_{12}$ to give $NaHRu_3(CO)_{11}$.

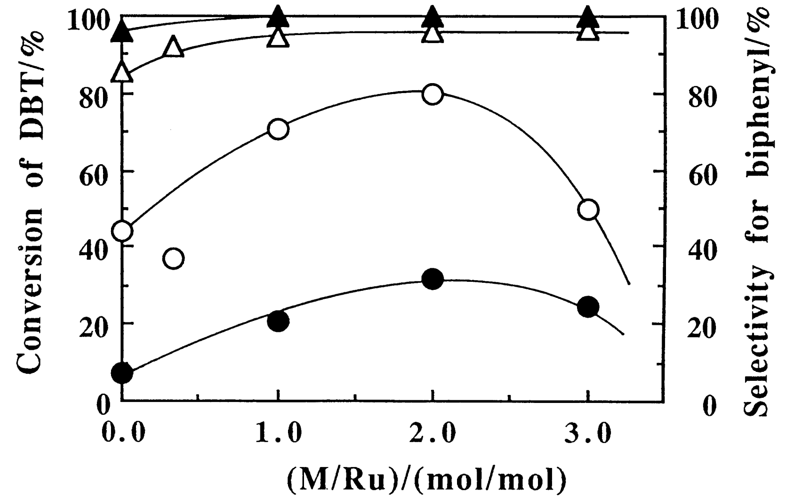

Fig. 2. Effects of M/Ru molar ratio on the conversion of DBT and the selectivity for biphenyl.
$Ru_3(CO)_{12}$+nMOH/Al_2O_3 (M=Na or Cs);
Conversion of DBT: ○ : Na; ● : Cs;
Selectivity for biphenyl: △ : Na; ▲: Cs;
React. Temp : Na: 300 °C; Cs: 240 °C; 50 kg/cm^2, H_2 18 l/h, LHSV 14 h^{-1}, 1 wt% of DBT in xylene, 3 h on stream.

When a kind of alkali metal was changed, the rate of HDS of DBT increased in the order Li<Na<K<Rb<Cs suggesting that the ion radius would affect the catalytic activity (Fig. 1). As shown in Fig. 2, the conversion of DBT and the selectivity for biphenyl increased with an increase in a M/Ru molar ratio (M=Na or Cs). The latter reached 100% when Cs was used at 240 °C. Further, the former showed the maximum at M/Ru=2 which was larger than the amount of alkali metal hydroxide needed for the formation of $MHRu_3(CO)_{11}$

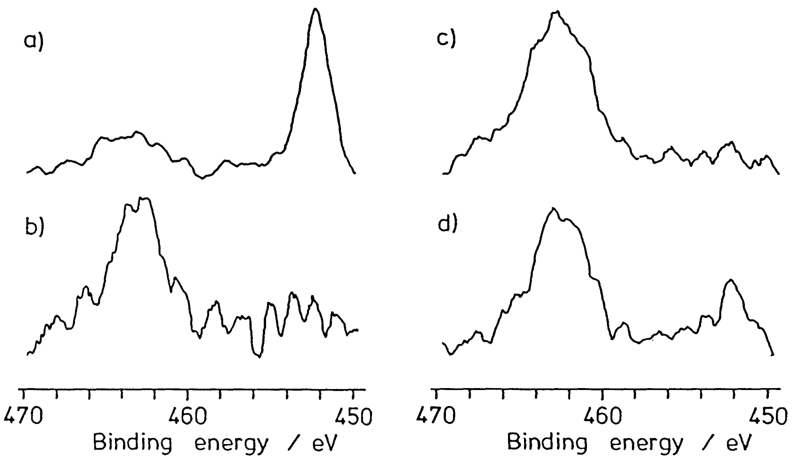

Fig. 3. Ru 3p3/2 XPS spectra of the catalysts derived from the alumina-supported ruthenium systems after the HDS reaction.
a) $Ru_3(CO)_{12}$+3CsOH/Al_2O_3; b) $Ru_3(CO)_{12}/Al_2O_3$;
c) Ru(AcAc)$_3$/Al_2O_3; d) $RuCl_3/Al_2O_3$; Etching time: 5.0 min.

(M/Ru=1), suggesting that excess of alkali metals were consumed by alumina. Figure 3 shows the Ru 3p3/2 XPS spectra of the used catalyst. The characteristic peak of the catalyst derived from the $Ru_3(CO)_{12}$+3CsOH /Al_2O_3 system was observed at 452.2 eV (Fig. 3a). Taking into account 3p3/2 XPS spectrum of Ru(0) (461.0 eV), it is deduced that ruthenium species in the catalyst may have much higher electron density than Ru(0). The Ru 3p3/2 XPS spectra from the alumina-supported $Ru_3(CO)_{12}$, $Ru(AcAc)_3$ and $RuCl_3$ systems showed peaks in the range 462.7-463.0 eV which can be assigned to RuS_2 (Fig. 3b, c, and d). The ratios of peak areas of Ru 3p3/2 and Al 2p in alumina-supported $Ru_3(CO)_{12}$+3CsOH, $Ru_3(CO)_{12}$, $Ru(AcAc)_3$ and $RuCl_3$ systems were 0.038, 0.032, 0.027, and 0.044, respectively. These results suggest that ruthenium species with the high electron density would be more active for HDS of DBT than RuS_2 supported on alumina and that such active species would be maintained on alumina by binding alkali metals.

The catalysts derived from conventional sulfided MoO_3/Al_2O_3 (MoO_3, 12.5 wt%/g-cat) and CoO-MoO_3/Al_2O_3 (CoO, 3.8 wt%/g-cat; MoO_3, 12.5 wt%/g-cat) exhibited 38 and 96% of the conversions in HDS of DBT at 300 °C, respectively. The former value was much smaller than that of the catalyst derived from a $Ru_3(CO)_{12}$+3CsOH/Al_2O_3 system while the latter was almost same. Further, the addition of alkali metals into MoO_3/Al_2O_3 and CoO-MoO_3/Al_2O_3 did not show a significant increase in the catalytic activity. The effects of alkali metals on hydrodesulfurization of thiophenes have been reported.12) However, there is a large discrepancy within the literature and no definitive conclusion has been obtained. On the other hand, although HDS of thiophenes using ruthenium sulfide catalysts were reported, the effects of addition of alkali metals on the HDS reactions have not been well-known in those catalysts. Further, it has been reported that the catalyst derived from supported $Ru_3(CO)_{12}$ showed the lower activity for HDS of thiophene than that from supported $RuCl_3$.5) In this communication, however, it has been clarified that the modification of $Ru_3(CO)_{12}$ with alkali metal hydroxides improved the properties of the catalyst obtained.

References

1) T. A. Pecoraro and R. R. Chianelli, *J. Catal.*, **67**, 430 (1981).
2) T. G. Harvey and T. W. Matheson, *J. Catal.*, **101**, 253 (1986).
3) P. C. H. Mitchell, C. E. Scott, J. P. Bonnelle, and J. G. Grimblot, *J. Catal.*, **107**, 482 (1987).
4) Y. Kuo, R. A. Cocco, and B. J. Tatarchuk, *J. Catal.*, **112**, 250 (1988).
5) J. A. de Los Reyes, S. Goeboeloes, M. Vrinat, and M. Breysse, *Catal. Lett.*, **5**, 17 (1990).
6) M. Lacroix, N. Boutarfa, C. Guillard, M. Vrinat, and M. Breysse, *J. Catal.*, **120**, 473 (1989).
7) For review: D. C. Bailey and S. H. Langer, *Chem. Rev.*, **81**, 109 (1981).
8) A. Ishihara, T. Mitsudo, and Y. Watanabe, *J. Jpn. Petrol Inst.*, **33**, 28 (1990), and references cited therein.
9) K. Chatacondu, M. L. H. Green, J. Qin, M. E. Thompson, and P. J. Weisman, *J. Chem. Soc., Chem. Commun.*, **1988**, 223.
10) Y. Okamoto, A. Maezawa, H. Kane, and T. Imanaka, *J. Mol. Catal.*, **52**, 337 (1989); M. L. Vrinato, C. G. Gachet, and L. de Mourgues, "Catalysis by Zeolite," ed by B. Imelik, Elsevier, Amsterdam (1980), p. 219.
11) B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. Suess, *J. Chem. Soc., Dalton Trans.*, **1979**, 1356.
12) I. Chen and D-W. Shiue, *Ind. Eng. Chem. Res.*, **27**, 1391 (1988); A. Lycourghiotis and D. Vattis, *React. Kinet. Catal. Lett.*, **21**, 23 (1982); M. Poleski, C. Gachet, and L. de Mourgues, *C. R. Seances Acad. Sci. Ser. 2.*, **293**, 361 (1981).

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